A COMPARISON OF SHALE GAS OIL DENITRIFICATION REACTIONS OVER Co-Mo AND Ni-W CATALYSTS

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INTRODUCTION

As the Nation's needs for additional sources of petroleum products become ever more pressing, a role of oil shale in the synthetic fuels industry becomes more probable. One of the problems in converting shale oil to hydrocarbon liquid products is the elimination of nitrogen from the shale oil. Nitrogen compounds not only impart undesirable properties to the finished products but their basic nature makes them effective poisons for the acidic catalysts used in petroleum refining.

An efficient means of eliminating nitrogen from shale oil is hydrodenitrification of the oil in the presence of a dual function catalyst. In a study of the denitrification of model nitrogen compounds over an Ni-W on Al_2O_3 catalyst, Flinn[1] reported that amines and anilines reacted readily to form ammonia, but indole was much less active, and quinoline was the most difficult to denitrify. Unfortunately, most of the nitrogen in shale oil has been found to be of the quinoline and indole types.[2]

In a previous study in this laboratory,[3] the relative rates of disappearance of the types of nitrogen compounds present in shale gas oil were studied using a Co-Mo on Al_2O_3 catalyst. The present paper uses those Co-Mo results and results from experiments using Ni-W on Al_2O_3 and Ni-W on $SiO_2 \cdot Al_2O_3$ to compare the selectivity of these catalysts in denitrifying the types of nitrogen compounds in shale gas oil. These comparisons should afford insight into the role of the catalyst during denitrification reactions.

EXPERIMENTAL

A gas combustion retort shale gas oil was hydrogenated in a 2-liter, externally heated, stirred reactor for 1/2 hour and for 3 hours at operating temperatures of 600°, 700°, 750°, and 825° F. Properties of this gas oil are listed in Table I. The initial hydrogen pressure was 3,000 psig and at operating temperatures pressures varied from 3,500 psig to 5,500 psig. Details of the operating procedure have been reported previously.[3]

TABLE I. – Properties of shale gas oil feedstock

Gravity, °API	21.5
Nitrogen, wt pct	2.00
Sulfur, wt pct	0.60
Boiling range, °F	515 to 900

Three different catalysts were used--Co-Mo on Al_2O_3 (Nalco, Nalcomo 471), Ni-W on Al_2O_3 (Nalco, NT 550), and Ni-W on $SiO_2 \cdot Al_2O_3$ (Harshaw, Ni-4301). The source and composition of these catalysts are presented in Table II and selected properties of the catalysts are presented in Table III. Although it was recognized that different catalysts require unique

TABLE II. - Source and composition of catalysts

| | Catalyst | | |
	Co-Mo on Al_2O_3	Ni-W on Al_2O_3	Ni-W on $SiO_2 \cdot Al_2O_3$
Supplier	Nalco Chemical	Nalco Chemical	Harshaw Chemical
Trade name	Nalcomo 471	NT 550	Ni-4301
Composition, wt pct	3.5 CoO	4 Ni	6 Ni
	12.5 MoO_3	16 W	19 W
	84.0 Al_2O_3	80 Al_2O_3	20 SiO_2
			55 Al_2O_3

TABLE III. - Selected catalyst properties

| | Catalyst | | |
	Co-Mo on Al_2O_3	Ni-W on Al_2O_3	Ni-W on $SiO_2 \cdot Al_2O_3$
Trade name	(Nalcomo 471)	(NT 550)	(Ni-4301)
Pore volume, cc/gm	0.40	0.35	0.20
Average pore radius, Å	35.1	35.7	19.5
BET area, m^2/gm	226.4	195.7	208.5

| | Pore-size distribution | | |
Pore radius, Å	Vol pct		
300-250	1.3	1.0	1.2
250-200	2.4	1.8	.7
200-150	4.0	3.0	1.1
150-100	8.5	7.6	2.3
100-90	2.7	2.8	.8
90-80	4.0	4.7	1.1
80-70	5.0	6.9	1.4
70-60	7.0	8.3	1.8
60-50	8.8	10.0	2.0
50-45	6.1	6.9	1.5
45-40	6.6	7.0	1.9
40-35	7.6	7.5	2.4
35-30	8.0	7.5	6.0
30-25	9.1	7.9	9.7
25-20	3.9	6.8	17.5
20-15	11.6	6.1	25.6
15-10	3.6	4.1	22.9
10-7	.0	.0	.0

pretreatment before use in order to maximize their individual activities, all three catalysts were given the same pretreatment in order to reduce the number of experimental variables. On the basis of work reported by Richardson,[4] who indicated that the desulfurization activity of the Co-Mo catalyst could be optimized by preheating at 1,000° F, it was assumed that the same pretreatment would optimize denitrification activity and all catalysts were preheated at 1,000° F for 2 hours and allowed to cool in a dessicator. The catalysts were then added to the reactor in the oxidized state where they were partially sulfided by means of the gas-oil desulfurization reactions occurring during the period in which the reactor was heated at a rate of 4° F per minute to reaction temperature.

Samples of the product oil from the reactor were analyzed for total nitrogen using the Kjeldahl method,[5] and for nitrogen types using nonaqueous, potentiometric titrations and infrared analyses as suggested by Okuno[6] and modified by Koros.[7] When the titration data were combined with the data from the infrared determination of indole-type compounds, it was possible to classify the nitrogen compounds into the following types: Quinolines (including pyridines, quinolines, acridines, and tertiary amines); arylamines (including 1,2,3,4-tetrahydroquinolines, 2,3-dihydroindoles, and anilines); indoles (including pyrroles, indoles, and carbazoles); primary and secondary amines; amides (including quinolones and oxindoles); and unidentified compounds. A complete discussion of the details of this classification procedure has been previously reported.[3,8]

RESULTS AND DISCUSSION

Table IV lists catalysts, temperatures, times, percent of the total nitrogen removed, and nitrogen types expressed as their weight percent of the total nitrogen remaining in the product oil. The data in Table IV show that the denitrification reactions were studied over the range of zero to 80 percent nitrogen removal and, with the exception of one instance, 90 or more percent of the total nitrogen was classified into one of the five nitrogen types.

The selectivity of each of the three catalysts toward converting each of these five types of nitrogen to either ammonia or to another nitrogen type was determined by plotting the nitrogen type in the product oil as a function of the total nitrogen removed in the denitrification reaction. If the slope of the resulting plot is positive, that nitrogen type is being converted at a slower rate than the rate at which total nitrogen is removed. If the slope is negative, the relative rate is faster.

Figure 1 is the resulting plot for the quinoline-type nitrogen using the three catalysts. The positive slope of the Co-Mo curve shows that the conversion of quinoline when Co-Mo is the catalyst proceeds at a slower rate than the rate at which total nitrogen is removed. The negative slope of the Ni-W curve shows that the quinoline is being converted at a faster, relative rate. Only one curve has been drawn through the two sets of Ni-W data because regression analyses of the Ni-W data showed very little difference when the four Ni-W on $SiO_2 \cdot Al_2O_3$ data points were added to the eight Ni-W on Al_2O_3 data points. This was true for the conversion of all five nitrogen types; hence, the Ni-W data were treated as one curve in all five cases.

Figure 2 is the resulting plot for the indole-type nitrogen. Indole-type nitrogen accounts for 15 percent of the feedstock nitrogen and at a nitrogen removal of 3 percent, when using the Co-Mo catalyst, it accounts for 19 percent of the nitrogen remaining in the liquid product. When the two Ni-W catalysts are used, indole nitrogen accounts for 18 percent of the remaining nitrogen even though there was not distinguishable removal of nitrogen from the liquid. These increased levels of indole-type nitrogen can only be accounted for by the conversion of other types of nitrogen to indole type. In a previous paper,[3] which reported Co-Mo results, we suggested that the amide type and unidentified type were the most likely sources of this increase in indole nitrogen. We now see the same selectivity when the two Ni-W catalysts are used.

TABLE IV. – <u>Nitrogen types in product oils</u>

Temp, °F	Time, hrs	Total nitrogen removed, wt pct	Nitrogen type, wt pct of total nitrogen remaining in liquid product					
			Quinoline type	Indole type	Aryl-amine type	Primary and secondary amine type	Amide type	Unidenti-fied
				Feed gas oil				
–	–	–	52	16	1	2	20	9
				Co–Mo on Al_2O_3				
600	1/2	3	53	19	5	7	11	5
	3	6	51	16	9	15	8	2
700	1/2	12	52	16	10	14	6	2
	3	32	54	14	13	12	4	3
750	1/2	26	53	13	12	14	4	4
	3	70	61	14	19	3	2	1
825	1/2	65	55	13	20	7	2	3
	3	1/ 95	–	–	–	–	–	–
				Ni–W on Al_2O_3				
600	1/2	0	51	18	4	2	15	10
	3	0	50	18	5	3	14	10
700	1/2	3	48	17	5	10	13	7
	3	12	46	13	7	16	11	7
750	1/2	16	48	14	7	15	13	3
	3	51	46	15	16	13	3	7
825	1/2	59	44	16	18	11	1	10
	3	79	41	17	25	6	1	10
				Ni–W on $SiO_2 \cdot Al_2O_3$				
700	1/2	2	49	18	4	7	16	6
	3	8	46	15	6	15	16	2
825	1/2	43	47	15	15	10	6	7
	3	75	37	15	29	3	4	12

1/ Not sufficient concentration to analyze product oil.

Figure 2 also shows that once the initial buildup of indole is over, its conversion to ammonia or to other nitrogen types is much faster than the overage conversion until about 25 percent of the denitrification reaction is completed. At this point indoles are converted more slowly when the Ni-W catalysts are used than when Co-Mo is used and in both cases, the rates are slower than that for total nitrogen removal.

A conclusion that can be reached from the results shown in figures 1 and 2 is, despite the compositional differences in the two Ni-W catalysts, there is little difference in their selectivity for the conversion of quinoline types and of indole types. These results do show that the selectivity of the two Ni-W catalysts is different than the selectivity of the Co-Mo catalyst for these

two classes of compounds. The Ni-W catalysts convert quinolines faster than do the Co-Mo and above 20 percent nitrogen removal the Co-Mo converts the indoles faster than do the Ni-W catalysts.

These selectivity results might be explained on the basis of differences in the adsorption characteristics of the catalysts due to differences in the acidity of the catalyst supports. Haensel[9] reports that the ability of a catalyst to adsorb nitrogen compounds is largely influenced by the acidity of the catalyst. However, the Ni-W on Al_2O_3 catalyst and the Ni-W on $SiO_2 \cdot Al_2O_3$ catalyst show the same selectivity but the chemical compositions of their supports as shown in Table II, are different. Further, as shown in Table III, the Co-Mo on Al_2O_3 catalyst and the Ni-W on Al_2O_3 catalyst are similar in their pore distribution patterns, yet their selectivities differ. Thus, it seems more likely that in this case the observed differences in selectivity should be attributed to the differences in the active-metal components, Co-Mo and Ni-W, rather than to the differences in the catalyst supports.

Figure 3 shows the relative percentage of the unconverted nitrogen compounds which have been classified as arylamine-type compounds (including hydrogenated quinolines, hydrogenated indoles, and anilines) as a function of the extent of the denitrification reaction. Arylamines can be formed by means of hydrogenation of quinoline-type and indole-type compounds and disappear by means of hydrocracking to form ammonia. These results show that, at the high hydrogen pressures used in this study, there is little difference in the three catalysts in their selectivity for converting arylamines. Also, the rate at which arylamines are formed by hydrogenation of quinolines and indoles over all three catalysts is more rapid than the rate at which the arylamines are converted by hydrocracking. This finding is substantiated by the work of Brown,[10] who reported that anilines comprised about one-third of the tar bases in a shale-oil naphtha produced by recycle hydrocracking of a crude shale oil. Even though the results presented in figure 1 show that the rate of hydrogenation of quinoline-type nitrogen compounds is slower than the rate at which total nitrogen is removed over the Co-Mo catalyst, the results shown in figure 3 suggest that the hydrogenation reaction does not completely limit the overall rate of denitrification over this catalyst even at 800° F as Koros[7] reported and as we have reported in an earlier paper.[4]

Figure 4 shows the relative percentages of the unconverted nitrogen compounds which have been classified as primary and secondary amines as a function of the removal of total nitrogen. Although we have shown two curves in this figure, a regression analysis showed that there is little difference in the Ni-W and Co-Mo data. Hence, there is little difference in the selectivity of these three catalysts in their ability to effect a conversion of the primary and secondary amines. Figure 4 shows that, at nitrogen removals up to about 20 percent, the relative percentages of primary and secondary amines increase significantly, but at higher nitrogen removals, these compounds are rapidly converted to ammonia.

Figure 5 is a plot of the data for amide-type nitrogen. As shown here, the relative percentage of amide nitrogen decreases rapidly at low nitrogen removal. The Co-Mo catalyst exerts a stronger influence than do the Ni-W catalysts in the conversion of amides at low nitrogen removals, but all three catalysts are quite effective in converting amide-type nitrogen to other forms.

SUMMARY

The selectivity of three catalysts (Co-Mo on Al_2O_3, Ni-W on Al_2O_3, and Ni-W on $SiO_2 \cdot Al_2O_3$) on influencing the conversion of five, identifiable types of nitrogen compounds has been demonstrated. The two Ni-W catalysts are somewhat more selective in converting quinoline-type compounds than is the Co-Mo catalyst. Because there is no difference in the selectivity of

the two Ni-W catalysts which differ from each other in the composition of their supports, it seems likely that the active-metal component of the catalyst is the determining factor in the selectivity of quinoline conversion. At low denitrification levels, all three catalysts are effective in rapidly converting indole-type nitrogen, but above 20 percent nitrogen removal, the Co-Mo catalyst is more effective than the Ni-W catalysts. All three catalysts show that they are less effective in converting arylamines than they are in removing nitrogen; and they show approximately the same selectivity toward primary and secondary amines. The Co-Mo catalyst converts amide-type nitrogen much faster at low levels than do the two Ni-W catalysts; but all three catalysts are highly selective in promoting conversion of amide-type nitrogen.

The results also show that the relative percentages of different nitrogen compounds change as shale gas oil is denitrified. At low and intermediate levels of nitrogen removal, all five types of nitrogen compounds are present in the liquid product. However, at higher levels of nitrogen removal, the identifiable nitrogen compounds remaining in the liquid product consist primarily of quinolines, indoles, and arylamines. Primary and secondary amines and amides are practically missing from the product at levels approaching 80 percent removal of nitrogen.

ACKNOWLEDGMENTS

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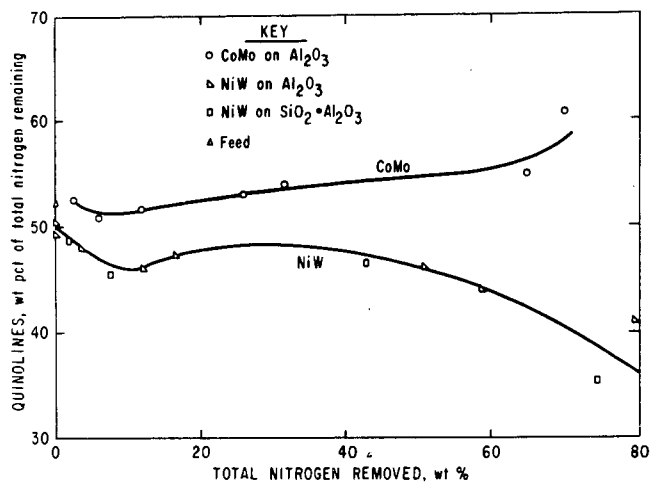10. Brown, Dennis, Earnshaw, D. G., McDonald, F. R., and Jensen, H. B., Anal. Chem. 42, 146 (1970).
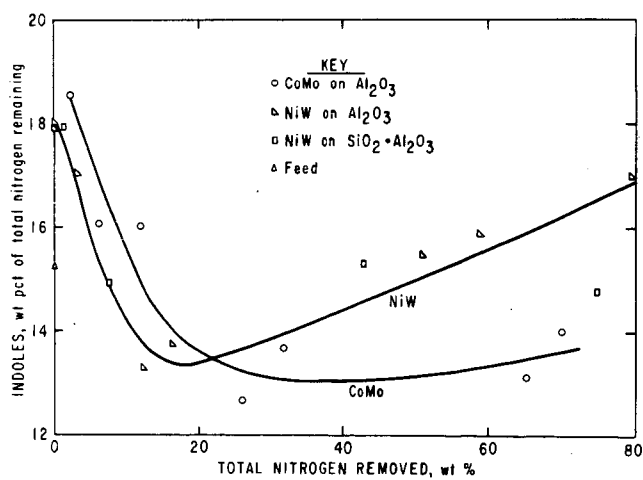
FIGURE 1.-Quinoline-Nitrogen Conversion.
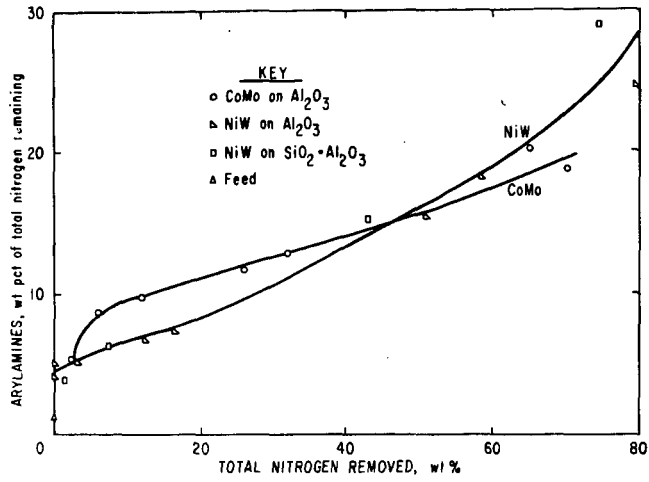

FIGURE 2.- Indole-Nitrogen Conversion.
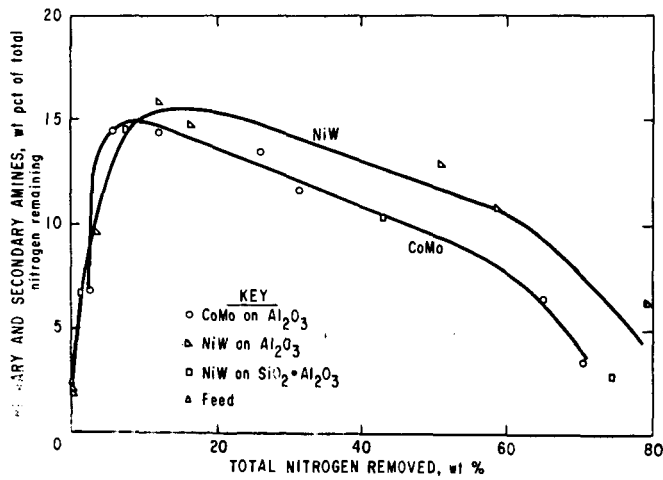
FIGURE 3.-Arylamine—Nitrogen Conversion.

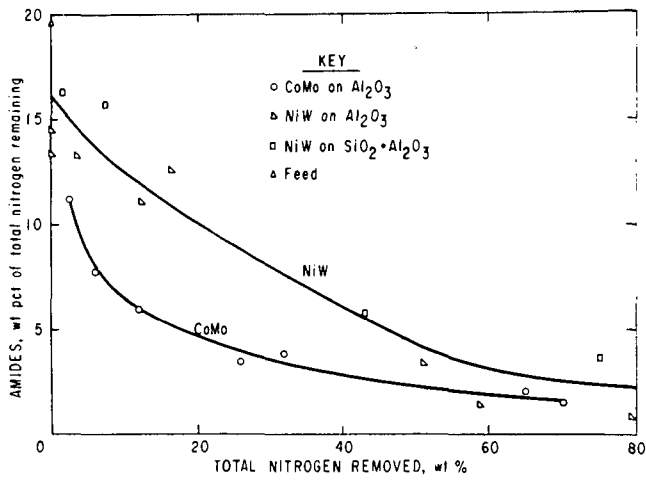
FIGURE 4.-Primary And Secondary Amine-Nitrogen Conversion.

FIGURE 5.–Amide-Nitrogen Conversion.